

Localized charged states and phase separation near second order phase transition

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Localized charged states and phase segregation are described in the framework of the phenomenological Ginzburg-Landau theory of phase transitions. The Coulomb interactions determines the charge distribution and the characteristic length of the phase separated states. The phase separation with charge segregation becomes possible because of the large dielectric constant and the small density of extra charge in the range of charge localization. The phase diagram is calculated and the energy gain of the phase separated state is estimated. The role of the Coulomb interaction is elucidated.

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There is a common belief that complex interactions between charge, spin, orbital, and lattice degrees of freedom may lead to inhomogeneous ground state with charge and phase separation. The role of these inhomogeneous states in the anomalous transport and magnetic properties in manganites[1, 2, 3, 4, 5, 6] and in high temperature superconductors [7, 8, 9, 10] is often discussed in literature. It was shown that inhomogeneous states may appear above Curie temperature and new characteristic temperature T^* was introduced[5, 7]. Note, that the tendency to the phase separation is widely discussed for manganites[4, 5, 6], as well as for high-temperature superconductors [7], microscopic origin of this anomalous behavior is far from understanding. The origin and the temperature range of this phenomena is still an open problem[3, 4, 5, 6, 8, 9, 10, 11]. In this paper we discuss the tendency and conditions of the formation of inhomogeneous states with the spacial charge localization and the phase separation within the phenomenological Ginzburg-Landau formalism and clarify the role of the Coulomb interaction in this phenomena.

The problem of spatially inhomogeneous states in the charged systems frustrated by the Coulomb interactions is constantly under debate for different systems [3, 4, 5, 6, 7, 12, 13, 14, 15, 16, 17, 18]. Usually the first order phase transition is considered where the charge density is coupled linearly to the order parameter (as an external field)[17] or to the square of the order parameter (local temperature)[18]. Very often the Coulomb interaction is discussed on the qualitative level or on the last stage of the calculations [6, 13, 14, 19]. The general method of consideration of the long-range Coulomb interaction for the two dimensional case was proposed in ref.[17, 18]. In the recent paper[19] the effect of the long-range Coulomb interaction to the second order phase transition was considered. However the Coulomb interaction was considered only for the special cases, where the density distribution was approximated in the attempts to minimize Coulomb contribution to the free energy[19], rather then it was obtained from the general formulation of the problem. In our opinion, The contribution of the Coulomb interaction is most important in the deter-

mination of the form of the inhomogeneous states and therefore we consider this interaction exactly.

Phenomenological approach to the theory of phase transition, proposed by V.L. Ginzburg and L.D. Landau indicates that the properties of the system near the phase transition are determined by the closeness to the phase transition point and weakly dependent on the other properties of the system. Therefore our results demonstrates that the properties of the spatially inhomogeneous states are determined by the closeness to the phase transition point, but not by the properties of the interactions in the system. We obtain the contribution of the Coulomb interaction to the thermodynamic potential of the inhomogeneous state and show that this contribution may be relatively small, to allow the phase separation. Note, that the phase separation is possible for the system displaying phase transition of the second order.

Let us consider doped system in the vicinity of the second order phase transition. We assume that the average concentration of the free carriers $\bar{\rho}$ is proportional to the dopant concentration \bar{x} . The thermodynamic potential $\Phi = \int \phi(\eta, \rho) dV$ describes the behavior of the order parameter η near second order phase transition and interaction of the order parameter with the charge density. Close to the phase transition it has the form:

$$\begin{aligned}\phi(\eta, \rho) &= \phi_0 + \phi_\eta + \phi_{int} + \phi_{coul} \\ \phi_\eta(\eta) &= \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{D}{2}(\nabla\eta)^2 \\ \phi_{int}(\eta, \rho) &= \frac{\sigma_1}{2}\eta^2\rho + \frac{\sigma_2}{2}\eta^2\rho^2 \\ \phi_{coul}(\rho) &= \frac{\gamma}{2}(\rho(r) - \bar{\rho}) \int \frac{\rho(r') - \bar{\rho}}{|r - r'|} dV'\end{aligned}\tag{1}$$

where ϕ_0 is the density of the thermodynamic potential in the high-temperature phase, ϕ_η is the density of the thermodynamic potential in the low-temperature phase, α , β , D are coefficients in the expansion of the thermodynamic potentials in powers of the order parameter ($\alpha = \alpha'(T - T_c)$, where T_c critical temperature in the absence of doping, $\alpha' = 1/C$, where C is the Curie constant), D is proportional to the diffusion coefficient.

Density of the thermodynamic potential ϕ_{int} describes the interaction of the order parameter with the charge, σ_1 and σ_2 are the constants of interactions (the term $\sigma_2\eta^2\rho^2$ is important to provide global stability of the system[14], $\sigma_2 > 0$). The density of the thermodynamic potential ϕ_{coul} describes charging effects due to long-range Coulomb forces, $\bar{\rho}$ is the average concentration of the charge. We assume that Coulomb contribution is the strongest. The effect of average dopant concentration $\bar{\rho}$ to the thermodynamic potential in the high-temperature phase is included in ϕ_0 . The coefficient γ is inversely proportional to static dielectric constant ε , $\gamma = 1/\varepsilon$. As a result the coefficients in the thermodynamic potential depend on charge density ρ and the term $\sigma_1\rho(1 + \rho\sigma_2/\sigma_1)$ determines the shift of the critical temperature of the phase transition due to local charge density. Therefore the influence of the electronic system on the phase transition manifests itself as a continuous shift of the critical temperature $T_{c\rho}$ with the change of the local charge density:

$$T_{c\rho}(\rho) = T_c - (\sigma_1\rho(1 + \sigma_2\rho/\sigma_1))/\alpha' \quad (2)$$

The local charge density may be different from $\bar{\rho}$ in some region of a finite size.

In the future we perform analysis for 3D case. The analysis for 2D case is similar. Equilibrium state of the system is determined by two equations: $\partial\phi(\eta, \rho)/\partial\eta = 0$, $\partial\phi(\eta, \rho)/\partial\rho = 0$. The second equation determines the dependence of the charge density ρ_0 on η :

$$\begin{aligned} \rho_0(\eta) &\simeq \bar{\rho} + \frac{\sigma_1}{8\pi\gamma}(1 + 2\sigma_2\bar{\rho}/\sigma_1)\nabla^2\eta^2 \\ &- \frac{\sigma_1^2}{32\pi^2\gamma^2}(1 + 2\sigma_2\bar{\rho}/\sigma_1)[(\nabla^2\eta^2)^2 + \eta^2\nabla^4\eta^2] \end{aligned} \quad (3)$$

Substituting Eq.(3) to Eq.(1) we obtain the expression of the thermodynamic potential (1) ϕ_{ρ_0} for the equilibrium distribution of the charge density $\rho_0(\eta)$:

$$\begin{aligned} \phi_{\rho_0}(\eta) &= \phi_\eta(\eta) + (\sigma_1 + \sigma_2\bar{\rho})\eta^2\bar{\rho}/2 \\ &- \frac{(\sigma_1 + 2\sigma_2\bar{\rho})^2}{32\pi\gamma}[(\nabla\eta^2)^2 - \frac{\sigma_2}{4\pi\gamma}\eta^2(\nabla^2\eta^2)^2] \end{aligned} \quad (4)$$

The negative sign in the third term of Eq.(4) $(-\nabla\eta^2)^2$ indicates that uniform state may be unstable towards inhomogeneous fluctuations. Similar instabilities were discussed in the case of first order phase transition in Refs.[17, 18].

This instability leads to spatially inhomogeneous solutions. Most simple solution is spherically symmetric. This equilibrium inhomogeneous state, obtained by computer minimization of the thermodynamic potential Eq.(1), has spherical form and plotted in Fig.(1). This results are obtained by applying the numerical technique described in Ref.[20]. This solution has characteristic size R_0 and characteristic charge density inside of this region ρ_0 under condition that average charge density in the system is equal to $\bar{\rho}$. It is clear that the charge is

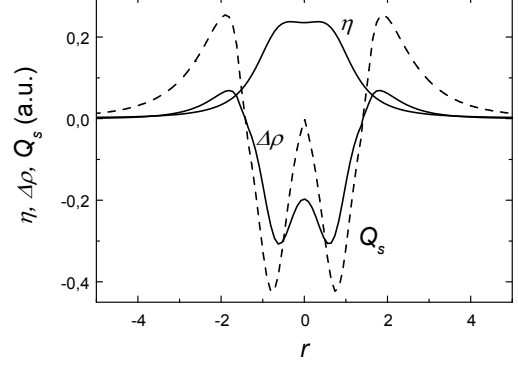


FIG. 1: (a) Spatial variations of the order parameter $\eta(r)$ and charge density $\Delta\rho(r) = \rho(r) - \bar{\rho}$ along the diagonal of the sphere in the equilibrium nonhomogeneous state, obtained by numerical minimization of the free energy; Q_s is integral concentration of the charge as a function of distance from the center of sphere ($Q_s = \Delta\rho(r)S_r$)

concentrated near the surface of the sphere. It allows to use approximation of the double electrical layer for calculation of the Coulomb energy. At large distances from the sphere the order parameter and the charge density are equal to their equilibrium values $\rho = \bar{\rho}$ and $\eta = \eta_s(\bar{\rho})$ ($\eta_s = 0$ or $\eta_s = -\tilde{\alpha}(\bar{\rho}, T)/\beta$). As a result the density of the thermodynamic potential ϕ_s for this solution we can write in the form:

$$\phi_s(R_0, x_0) = \phi_0 - \frac{A(x_0)}{3}R_0^3 + \frac{B(x_0)}{2}R_0^2 + \frac{K(x_0)}{4}R_0^4 \quad (5)$$

Here we use dimensionless concentration x instead of charge density ρ ($x = \rho a^3/e$, a is the lattice constant, and e is elementary charge) and \bar{x} corresponds to the level of doping. The coefficients in this formula are defined as follows: $A(x_0) = \pi(\tilde{\alpha}(x_0, T))^2/\beta V_0$, $B(x_0) \simeq 8\pi D(-\tilde{\alpha}(x_0, T))/d\beta V_0$, $K(x_0) \simeq \gamma e^2 dF(\bar{x} - x_0)^2/a^6 V_0$ ($\tilde{\alpha}(x_0, T) = \alpha(T) + \tilde{\sigma}_1 x + \tilde{\sigma}_2 x^2$, $\tilde{\sigma}_1 = e\sigma_1/a^3$, $\tilde{\sigma}_2 = e^2\sigma_2/a^6$, F is dimensionless factor which determines charge distribution $F = 4a^6 \int \phi_{coul} dV/\gamma e^2 R_0^4 d(\bar{x} - x_0)^2$, $F = 1/18$ in the limit of the double electrical layer, V_0 is the elementary layer that contains one sphere ($V_0 = V/n$ where n is the number of spheres), d is the thickness of the interphase boundary. Note, that Eq.(5) is valid if characteristic dimension of the nano-regions is larger than characteristic length $\xi = \hbar v/k_B T_{c\rho}(x_0)$, where \hbar is the Plank's constant, k_B is the Boltzmann constant, v is the characteristic velocity of the problem (in the case of structural phase transitions it is equal to the sound velocity and in the case of electronic phase transitions it is equal the Fermi velocity). This may be achieved relatively easy if $T_{c\rho}(x_0) > 10K$. Here we take into account the strong screening of the localized charges and write the energy in the double electrical layer approximation. In that case it is proportional to dR_0^4 . If the screening is absent this energy is proportional to R_0^5 [7]. The param-

eters $A(x_0)$ and $B(x_0)$ depend on temperature T , and parameter $K(x_0)$ depends on the average charge density \bar{x} . Parameters (\bar{x}, T) are external and we find the phase diagram in the space of these parameters. Since \bar{x} is determined by the level of doping, we study the change of the properties of the system with doping.

The conditions for the minimum of the potential $\phi_s(R_0, x_0)$ as a function of R_0 and x_0 and the condition that minimum of the potential is lower then the potential of the uniform state $\phi_s < \phi_0$ define the following set of equations:

$$\partial\phi_s(R_0, x_0)/\partial R_0 = 0 \quad (6)$$

$$\partial\phi_s(R_0, x_0)/\partial x_0 = 0 \quad (7)$$

$$\phi_s = \phi_0 \quad (8)$$

These equations define the upper boundary of the existence of the inhomogeneous state. Eq.(6) defines the equilibrium size of the charged domain R_0 :

$$R_0 = \frac{A(x_0)}{2K(x_0)} \left(1 + \sqrt{1 - \frac{4K(x_0)B(x_0)}{A(x_0)^2}}\right) \quad (9)$$

On the upper boundary of the region of the inhomogeneous states (Eq.(8)) we obtain the localization radius $R_0 = 2A(x_0)/3K(x_0)$. As a result Eq.(8) gives the following equation for x_0 as a function of temperature T :

$$\tilde{\alpha}(x_0, T)(\sigma_1 + 2\sigma_2 x_0)^2 + \frac{16\gamma e^2 \beta F D}{\pi a^6} = 0 \quad (10)$$

Using Eqs.(10) and (7) we write equation for upper boundary of the inhomogeneous states in the space of external parameters (\bar{x}, T) (the sign \pm is determined by the sign of σ_1):

$$\bar{x} = x_0(T) \pm \left(\frac{\pi a^6}{36\gamma e^2 \beta F D}\right)^{1/2} \tilde{\alpha}^{3/2}(x_0(T), T) = 0 \quad (11)$$

These equations define the temperature T_{ps1} of the transition to the region of stable inhomogeneous states in the space of external parameters (\bar{x}, T) ($T_{ps1} = f_1(\bar{x})$) where the energy of this inhomogeneous state is lower then the energy of homogeneous state. Similar consideration leads to the equation which defines lower boundary of the inhomogeneous states $T_{ps2} = f_2(\bar{x})$. Note that lower boundary T_{ps2} will be always close to the temperature $T_{c\rho}(\bar{x})$, because we do not gain, but contrary loss in energy ϕ_η when the bubble of the high-temperature phase is formed ($\phi_\eta(\eta = 0) = 0$, and $\phi_\eta(\eta_0) < 0$). It leads to the considerable difference between the formation of the bubble with the low-temperature phase in the high-temperature region and the bubble of the high-temperature phase in the low-temperature region. The first one is energetically favorable and therefore the region of the existence of this bubbles is considerably larger. It is important to note that Eqs.(10,11) which determine the phase diagram do not depend on d . This fact allows us to avoid optimization of our analysis with respect to d .

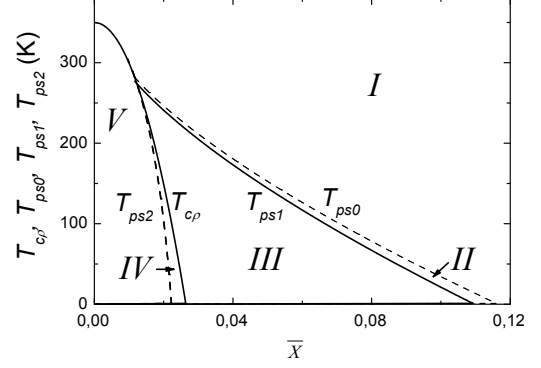


FIG. 2: Phase diagram of the system with $T_c = 350K$, $\sigma_1/\alpha' = 50K$, $\sigma_2/\alpha' = 510^5 K$, $\gamma e^2 \beta F D / \pi a^6 \alpha' = 2.33 T_c^3$: I is the region of the stable high-temperature phase; II is the region of the stable high-temperature phase with metastable bubbles of the low-temperature phase; III is the region of the stable inhomogeneous phase and metastable homogeneous high-temperature phase; IV is the region of the stable inhomogeneous phase and metastable uniform low-temperature phase; V is the region of the stable uniform low-temperature phase.

Typical phase diagram of the inhomogeneous state is presented in Fig.2 for the case of positive $\sigma_1 > 0$. Phase transition to the nonhomogeneous state represents typical phase transition of the first order. Metastable inhomogeneous phase appears at the temperature T_{ps0} which is much higher then the temperature of phase transition and it is shown in the phase diagram by dashed line. This line is determined from the conditions Eqs.(6,7) and $A(x_0)^2 = 4K(x_0, \bar{x})B(x_0, \bar{x})$ instead of Eq.(8). The characteristic size of the charged regions in that case is determined by the condition $R_0 = A(x_0)/2K(x_0, \bar{x})$.

Very often the Coulomb energy is estimated as $e^2/a \simeq 4eV$, which corresponds to two elementary charges localized in neighboring unite cells. However in our case to make the phase separation possible it is sufficient to have only small variation of the charge density per unite cell in comparison with average charge density $a^3(\rho_0 - \bar{\rho}) \simeq 0.1 - 0.2e$. Therefore we can estimate the Coulomb contribution to the free energy u_ρ as well as the energy gain due to formation of the low-temperature phase u_η (the second and the forth terms in Eq.(5)) per one unite cell in the nonhomogeneous phase $u_i = 3|\phi_i|a^3V_0/4\pi R_0^3$. We assume that d is small and neglect surface term in Eq.(5). For the Coulomb contribution we obtain:

$$u_\rho = \left(\frac{3e^2(x_0 - \bar{x})^2}{4\pi\epsilon a}\right) \frac{dR_0F}{a^2} \quad (12)$$

The characteristic energy in the brackets is of the order $u_0 = 0.0003 - 0.001eV$, here we use static dielectric constant $\epsilon = 30 - 40$, which is consistent with the measurements on manganites and high-temperature superconductors. The increase of the bubble size leads to

the increase of the energy u_ρ by the order of magnitude or more in comparison with u_0 , but on the other hand geometrical factor F decreases u_ρ . ($F = 1/18$ in the limiting case of the double electrical layer). Therefore u_ρ is evaluated as $0.003 - 0.01eV$. The corresponding estimate for the energy gain due to formation of the low-temperature phase is $u_\eta \simeq 3k_B T_c/4$ ($u_\eta \simeq a^3(\tilde{\alpha}(x_0, T=0))^2/4\beta \simeq a^3 T_c \eta_0^2(x_0, T=0)/C$, where $C = N(\eta_0(T=0)a^3)^2/3k_B$ and $N = a^{-3}$). Therefore $u_\eta \simeq 0.02 - 0.05eV$ for $T_c \simeq 270 - 700K$. Therefore in our case the phase separation becomes possible. The typical length scale of the nano-regions is estimated as $R_0 \simeq 1 - 20nm$.

The analysis of the pair distribution function obtained by neutron scattering shows that the charge density in manganites is localized on the scale of 3 to 4 interatomic distances. This is the case even if holes are localized in the form of polarons[5, 21]. It confirms that holes are localized not in the form of well separated polarons but in the form of nanoregions with finite charge density of polarons. The extra charge in that case is not more than $0.1 - 0.2e$ per unite cell. This is in consistence with our estimates. This state is characterized as the state with nano-dimensional charge and phase separation. Dynamics of these charged nano-regions may lead to high value of the dielectric constant in the low frequency range [11].

Therefore we have shown that the second order phase transition with critical temperature equal to zero at the certain doping (quantum critical point) is unstable with respect to formation of the spatially inhomogeneous charged states. Within the phenomenological Landau theory we have shown that these states appears at some temperature T_{ps1} , which is substantially higher

then the temperature T_{cp} (Fig.2). As a result the phase transition becomes effectively first order phase transition. Note that the Coulomb interaction determines the charge distribution, the screening and the characteristic length scale of the nonhomogeneous states. The spatially inhomogeneous state becomes possible in the systems with the large dielectric constants (30-40) and with relatively small charge density variations. The nonhomogeneous states were discussed also in the case of the phase transitions of the first order[17, 18]. However in that case spatial variations are related to the existence of two minima in the free energy in the region of hysteresis of the first order phase transition. In our case the nonhomogeneous states are related to the spatial charge redistribution.

In conclusion we note that the localized charged states and the phase separation appears even in the case of the second order phase transition. Properties of these states are described within the phenomenological theory of the phase transitions. The Coulomb interaction determines the spatial charge distribution, the screening and the characteristic length of charge localization. The charge and the phase separation becomes possible because of large dielectric constants and relatively small spatial variation of the charge density. We derive phase diagram and estimate different contributions to the free energy.

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